THERMAL INDICATING PAINTS FOR AMMUNITION ASSURANCE

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ABSTRACT

Ammunition is often exposed to extreme temperatures and solar radiation during transport, storage and pre-positioning. This is of particular concern in the present theater of operations. There have been documented incidents of failures caused by thermal exposures during Desert Storm and the recent Middle East conflicts. Currently there is no way to know what environmental extremes fielded items have experienced. An easily readable indication of the environmental exposure history of an item will enable troops and munitions managers to readily identify ordnances that may have been compromised. Furthermore, compromised munitions can be screened out to ensure mission success and enhance soldier safety.

Thermochromic polymers that change color in response to external stimuli can be utilized to monitor the temperature range and elapsed time profiles of stored and pre-positioned munitions. These polymers are being tailored to create inks, paints, and coatings that will alert Army logistic staff of dangerous temperature exposures. The resulting active coating can be visually inspected to determine if safe temperatures were exceeded.

Having an indication of the environmental exposure history of an item will enable troops and munitions managers to readily identify ordnances that may have been compromised. The use of thermally active paint systems accomplishes these objectives and assists the development community to address potential vulnerabilities.

1. INTRODUCTION

Present military operations often expose our assets to extreme temperatures and solar radiation. Transportation, storage and pre-positioning can potentially expose ammunition and other sensitive items to temperatures beyond design limits. There have been documented incidents of failures caused by thermal exposures during Desert Storm and the recent Middle East conflicts.

It was documented during Desert Storm operations that temperatures inside munitions' containers exceeded 190^{o}F degrees (PEO Ammo, PM JS AMMOLOG). This significantly exceeds the design limits of 145^{o}F – 165^{o}F. As an example of the potential deleterious impacts, when propelling charges are exposed to elevated temperatures for extended periods of time, the propellant stabilizer can be rapidly depleted. The potential for auto-ignition exists once all of the stabilizer is depleted. Furthermore, elevated gun pressures beyond safe operational limits can occur when propellants are fired beyond safe operating temperatures.

Currently there is no way to know what environmental extremes fielded items have experienced. Active coatings research at the U.S. Army's Armaments Research Development and Engineering Center (ARDEC) is working towards solutions to address these issues. Advances in chemistry and coatings development allows for an easily readable indication of the environmental exposure history of an item. This will enable troops and munitions managers to readily identify ordnances that may have been compromised. Furthermore, compromised munitions can be screened out to ensure mission success and enhancing soldier safety.

2. BACKGROUND

As previously mentioned ammunition is often exposed to extreme temperatures, solar radiation, and humidity during transport, storage, and pre-positioning. This is of particular concern in present theater of operations. The effects of these parameters may cause the ammo to reach temperatures that are in excess of the safe operating and storage conditions for these items. These circumstances are known to lead to degradation of propellant stabilizers, potential auto-ignition, elevated gun pressures, loss of munitions' functionality, decrease in reliability, and numerous safety issues.

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Since it is known that thermal exposure is harmful to munitions, designers and manufactures have been using previously developed Military Standards for assessing the functionality and survivability of Systems and Ammunition (Department of Defense MIL STD 810F, 2000). These standards cover potential operating and storage environments and were developed to cover 99% of global operational environments. Unfortunately the conditions in the Middle East are often out of this range. An assessment of the environment in Iraq recorded temperatures as high as 115^{o}F–125^{o}F with 1.0 kW/m^2 of insolation (Skelton et al., *Assessment of the Impact of Iraq Environment on Army Materiel.* Report for Army Corrosion Office. June 2005). Average daytime temperatures ranged from 95^{o}F–105^{o}F. Large diurnal cycles occur in the summer because of the inability of the dry air to retain temperature. The conditions are worse for items left out in the sun and inside containers. Temperatures have approached 200^{o}F.

The operational, transportation, and storage environments military munitions are exposed play a critical role in the safety and reliability of these assets. There are documented studies and reports listing potential high risk munitions items, failure modes, failure mechanisms, and safety concerns attributed to munitions exposed to extreme thermal conditions.

2.1 Current Practices

Current practices are to store munitions at depots, in igloos, warehouses, tents, etc. While depots and storage igloos are temperature monitored, individual rounds and containers are not. There can be extreme variations depending on location within a storage environment. In theaters of operations, temporary storage areas are set up, with little or no monitoring. Tents often tramp heat inside or blow over and leave the items exposed to increased thermal radiation.

The transportation and storage experience of rounds are often assumed or estimated; no real data is known or tracked. Thermometers and sensors are often used to monitor lots, but real individual exposures are unknown. Also as items move and are separated into sub-lots and change locations, the little information that was known is lost.

Soldiers know that exposure to environmental extremes are harmful to munitions. One approach often taken to mitigate this effect is to “dig” to obtain rounds from “the middle” of containers assuming they were less exposed than those on the top or edges. The problem is the next soldier comes along assuming that he/she should also “dig” to the middle but now the selected rounds were possibly those exposed to the higher temperatures from the top and edges.

2.2 Army Need for Munitions’ Monitoring

Based on these current operational problems, there is a need to monitor the thermal exposure of ammunition items. There are temperature ranges that ammo may encounter that can greatly decrease the safety and reliability of the round.

It is not uncommon for military munitions to endure extended storage, which may be greater than 20 years, in extreme environments. The operational, transportation, and storage conditions in extreme conditions pose tremendous challenges. Mission profiles for Army munitions systems often include operation in harsh environments which may include any or all of the following:

- Continuous operations in high humidity & moisture
- Continuous operations in areas of high wind
- Continuous operations in areas of high heat
- Extreme high & low pressured environments
- Large variations and rapid changes in temperature due to diurnal cycles and deployment from aircraft

An example of the affects of prolonged thermal exposure involves the 30 MM High Explosive ammunition family. The type of propellant for this ammunition family is susceptible to explosive degradation caused by prolonged thermal exposure above ~160^{o}F. Other ammunition families, including 25 MM rounds, are currently being assessed to determine the effects of prolonged thermal exposures since they contain similar powder configurations.

Army ammunition specialists have requested a sensor solution to monitor dwell time. A method is needed that can “remember” prior day exposures to aggregate 3 days of 2 hour exposures above 165^{o}F. Most sensor systems that have been considered are “intrusive” and change the shape/profile of the material they are placed on. Also the extend periods of dormant storage and prolonged transportation make powered devices and electronics impractical.

A cheap, easy, visible warning, requiring no power, which can be cost effectively applied to munitions and containers is desired by the warfighter. PEO Ammo requirements include monitoring of several temperature ranges including, 145^{o}F - 164^{o}F, 165^{o}F - 184 ^{o}F, and over 185 ^{o}F exposure. Figure 1 shows a proof of concept thermal coating developed for the Army.

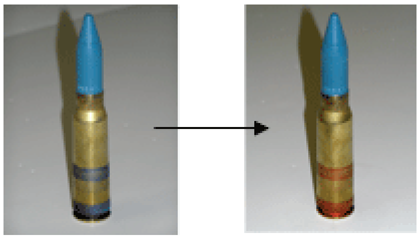

Fig 1. 50 Cal. Round after exposure over 157^{o}F (Zunino, 2007)

3. DEVELOPMENT OF THERMAL INDICATING PAINTS

3.1 Chromic Materials

Materials that change in response to external stimuli are of great interest to the Army and Department of Defense. Chromic polymers and materials are being used to develop thermal indicating paints of interest to the U.S. Army. Chromic materials refer to materials which radiate color, lose color (go translucent/transparent), or just change properties induced by external stimuli. Different stimuli cause response in different materials. "Chromic" is a suffix that means color, so chromic materials are named based on the stimuli energy affecting them, for example:

photochromic - light
thermochromic – heat
piezorochromic – pressure
solvatechromic – liquid
electrochromic – electricity/voltage

An example of thermochromic paint was demonstrated by Mattel Toy Corp. in the 1980's with Hot Wheels Color Racers® and Color FX™ cars (Katz, 2002). These cars were painted with temperature sensitive paint and which changed colors when placed in icy cold or warm tap water. These chromic paints change then changed back to their initial state once the stimuli were changed or removed.

Similar to Mattel, the researcher involved with the Army's Active Coatings Technologies (ACT) Project developed numerous chromic materials that change color to alert of a problem or anomalies in substrates, materials, and systems. Then they either changed back to their initial state once the stimuli was removed, or remained in a new physical state to mark or record a stimulus event.

To address the Army's requirement for thermal monitoring of munitions, the thermochromic polymers were needed that change color in response to external heat and radiation. These polymers are tailored to create inks, paints, and coatings to alert Army logistic staff of dangerous temperature exposures.

3.2 Polydiacetylenes (PDAs)

The primary monomers used to develop these thermal indicating coatings were Polydiacetylene (PDAs). Research on the properties of PDAs has been mainly focused on their large nonlinear optical response that originates from the long conjugated backbones (Wolfet et al., 1997). Besides their non-linear response, they exhibit photoinduced chromic transitions. Therefore, in the case of these monomers external stimuli result in polymerization, and in the polymer phase, changes in the backbone conformation are initiated (Iqbal et al., 1987).

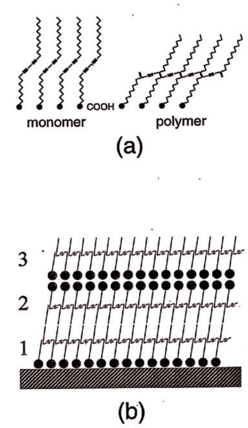

Fig. 2 (a) Chemical structural change of PDA monomer to polymer; (b) Crystalline ordering of extended blue phase which become red on distortion. Time-dependent change of red phase to a purple phase can occur under special conditions. (Iqbal, "Multiband Thermal Paints," Report for U.S. Army ARDEC, 2006).

These monomers are typically colorless and become increasingly colored with polymerization. Color in PDAs occurs as a result of π to π^* electronic transitions associated with the C≡C-C≡C diacetylene backbone shown in Figure 2. Reversible changes in the color of the polymer occur due to molecular conformational changes resulting from modifications of the side chain packing, ordering and orientation. This also means that these PDAs will undergo phase changes in two stable states, the blue state and the red state.

The utilization of thermochromic polydiacetylene (PDA) precursors is the basis of an active thermal indicating paint. Research and studies on numerous PDAs were conducted and evaluated as the color-active component in the paint formulations. Some PDAs considered for their blue to red transitions are illustrated in Figure 3 (Lee and Kim, 2007).

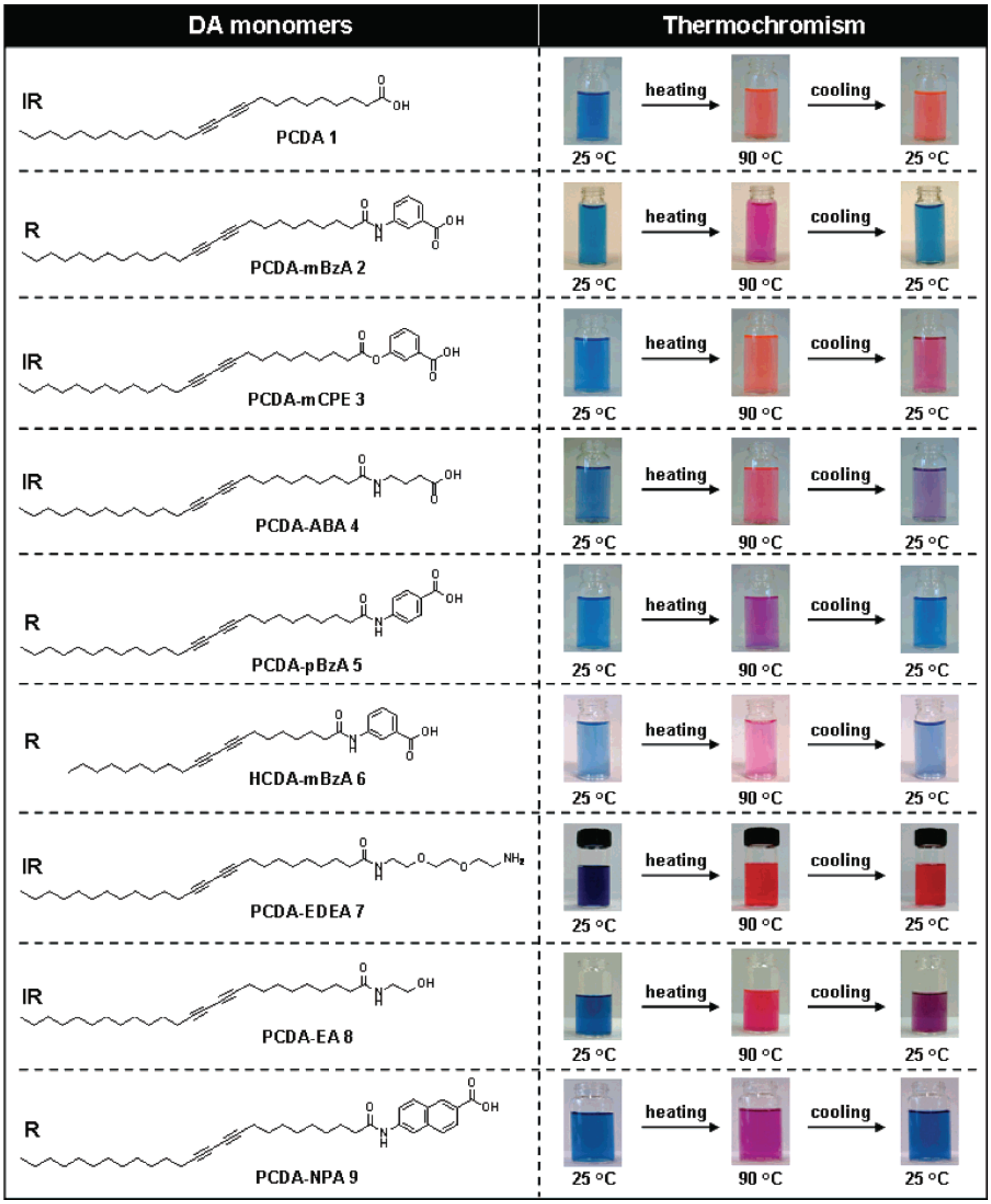

Fig. 3. Diacetylene monomers of PDA solutions that display irreversible (IR) or reversible (R) thermochromism (Lee and Kim, 2007).

In order for thermal indicating paints to be an acceptable solution for the Army, the overall cost versus added utility must be acceptable. If the coating is too expensive or too difficult to apply, it will not be practical and the Army will not implement. Therefore, cost-effective PDAs were analyzed and down selected for use in prototype active coatings.

A cost-effective, commercially diacetylene monomer, 10,12-pentacosadiynoic acid (PCDA), with an irreversible blue to red transition at 145°F (63°C), chemical formula: $CH_3(CH_2)_{11}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_8\text{-}COOH$ and 10,12-docosadiynedioic acid Bis-1, with an irreversible blue to red transition at 172°F (78° C), chemical formula: $HOOC\text{-}(CH_2)_8\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_8\text{-}COOH$ which dissolve in common solvents, serve as the basis for creating the desired paints.

Another important factor is the phase reversibility of the PDAs. Chemical methods can be used to control the reversibility of thermochromic materials. In PDAs the aromatic interactions between the head groups can be modified to control the amount of reversibility of the polymers or even make the polymer irreversible if desired. Strong head group interactions involving both H-bonding and aromatic bonding lead to reversibility. While some scientists disagree on the best methods to control the factors affecting reversibility, methods exist to modify or customize PDAs to achieve desired results.

A Raman study of the PCDA (Carpick et al., 2000) showed that a conformational change of alkyl side chains are constricted by hydrogen-bonded head groups which imposes a strain on the polymer backbone and finally leads to a drastic, irreversible change in the pi-electron conjugation length as one goes from the highly conjugated blue to the less conjugated red phase. The irreversibility of the red phase of the selected PDAs is of interest since it allows a “memory” of the conditions the material was exposed to be obtained.

Recent research by Lee & Kim at Hanyang University, Korea (Lee and Kim, 2007) uncovered an interesting phenomenon. They observed that CD-cyclodextrin disrupts head group interactions and therefore stabilizes red phase irreversibility; illustrated in Figure 4.

While several PDAs exhibited the desired irreversibility, PCDA was shown to have a brighter color contrast in its blue to red transitions, as illustrated in Figure 5, than Bis-1. However, co-crystals of PCDA and Bis-1 have been shown to have good color contrast and reproducible transition temperatures (Patel, 1980). The formation of the blue polymeric phase was found to be rapidly induced by ultraviolet irradiation for these PDAs.

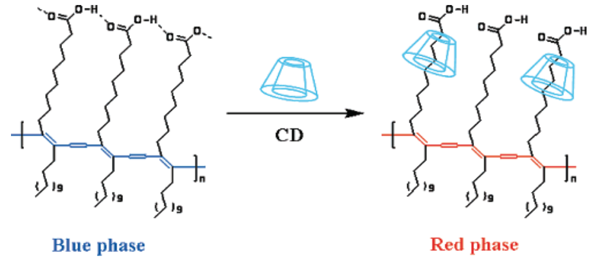

Fig. 4. A schematic representation of the interaction between PDA and CD (Lee and Kim, 2007).

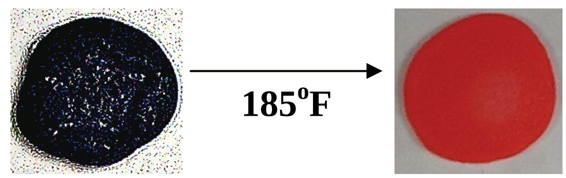

Fig. 5. PCDA optical transition after 185°F exposure (Zunino, 2007)

Since the resulting paints and coatings are being developed to alert if items were exposed to temperature extremes, it is critical that there is an irreversible transition and a high contrast visual change. Thermochromics that revert once the stimuli are removed or whose color fades would be useless for the Army’s potential applications.

3.3 Paint Formulations for Munitions Applications

For munitions applications of thermochromics several issue had to be addressed. While PDAs, including PCDA, Bis-1, Bis-2, etc, are the base materials, for use on munitions they are blended in different proportions with ultra-violet radiation blockers and polymers like polyurethanes, polyvinylpyrollidone (PVP), ethyl cellulose, polyvinyl alcohol (PVA), and polyvinylidene fluoride (PVDF) to form paints that irreversibly change color in the desired temperature ranges.

The PDA monomer in the painted-on coating is initially polymerized by UV radiation. Chemical modification of the monomers caused by changes in the composition of the formulation provide the different temperature bands to meet Army requirments. The elapsed time after temperature exposure can be measured by decrease in the intensity of the fluorescence of the red phase (using a hand-held optical sensor) due to the time-temperature induced formation of a blue polymeric phase with reduced fluorescence from PDA or similar monomers added to the formulation.

Ammunition is comprised of numerous different substrates; therefore, application methods, material compatibility, and paint survivability must be investigated. Compatibility and adhesion to metals, composites, and current military coatings must be determined and the paints/coatings cannot degrade or affect the performance of the munitions items.

Indicator formulations are being developed to optimize compatibility with organic resins present in complex organic coatings used on Army Materiel as well as for compatibility with numerous organic and inorganic substrates.

Another issue is the tunability of the base organic indicators to be irreversibly "trip" over narrow and well separated temperature bands between 100°F – 200°F. The base PCDA, Bis-1, Bis-2 and their co-crystals provided irreversible transitions within the desired ranges, 145°F - 164°F, 165°F - 184 °F, and over 185 °F.

Research highlights demonstrated that adding different materials and modifying the formulations could produce the desired results. Adding cellulose to the coating matrix improves paint homogeneity and increases the transition temperature of PCDA diacetylene in the formulation. Mixing PCDA with Bis-1 sharpens the transition to a lower temperature band and different ratios are being used to "tune" the paints for desired ranges. This is done by dissolving either PDA monomers singly or as co-crystals in organic solvents, usually alcohols. By preparing different suspensions/solutions of various concentrations of PVA, cellulose, and PVDF in organic solvents the trigger temperatures can be modified.

Prototype coatings systems were developed using different formulations for proof or concept testing. Three paint bands were added to "test panels" pre-coated with Chemical Agent Resistive Coating (CARC). Different formulations were used to determine the best base formulations for active coatings that "trigger" at desired temperatures. Each set of panels were exposed to increasing temperature in 10°C increments in an oven with a thermocouple at 0.5 hour increments. The cycle began at 50°C and stepped up to 130°C. Figure 6 illustrates the thermal stepping procedure used. The panels were removed from the oven, photographed, inspected under a microscope, and placed back in the oven after each step.

As predicted the thermal indicating bands converted from blue to red in color. While all of the bands transitioned, there were slight differences in "trigger" temperature and coating uniformity. Figures 7, 8 and 9 show the results of some of the test panels (Zunino and Iqbal, 2008, Thermal Paint Test Reports, U.S. Army ARDEC).

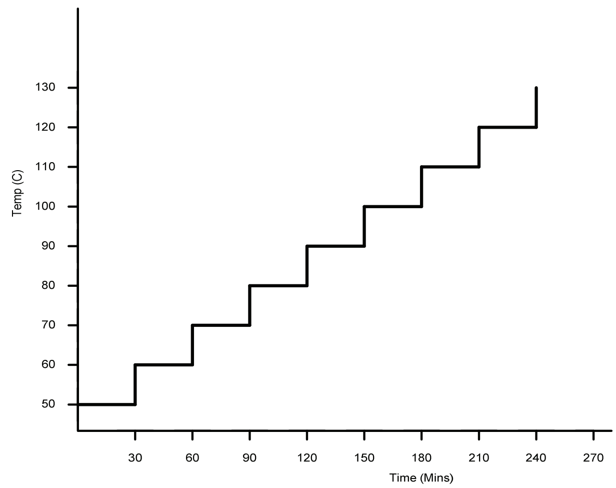

Fig.6. Thermal stepping for thermal paint testing.

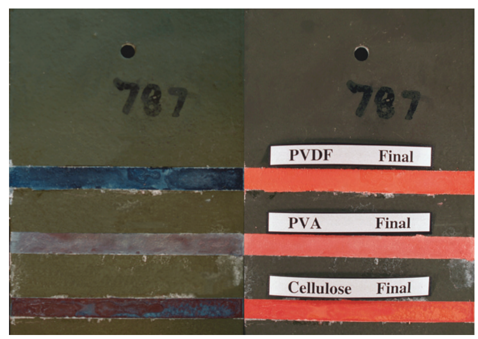

Fig. 7. Sample test panels with different base formulations before and after thermal stepping.

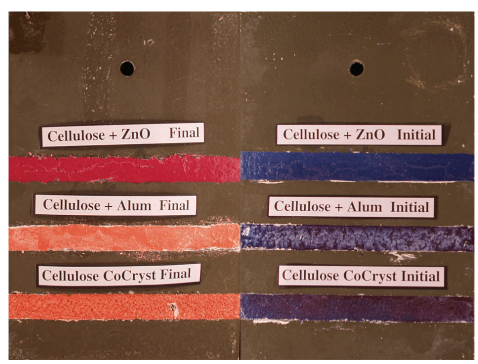

Fig. 8. Sample test panels with cellulose based formulations before and after thermal stepping.

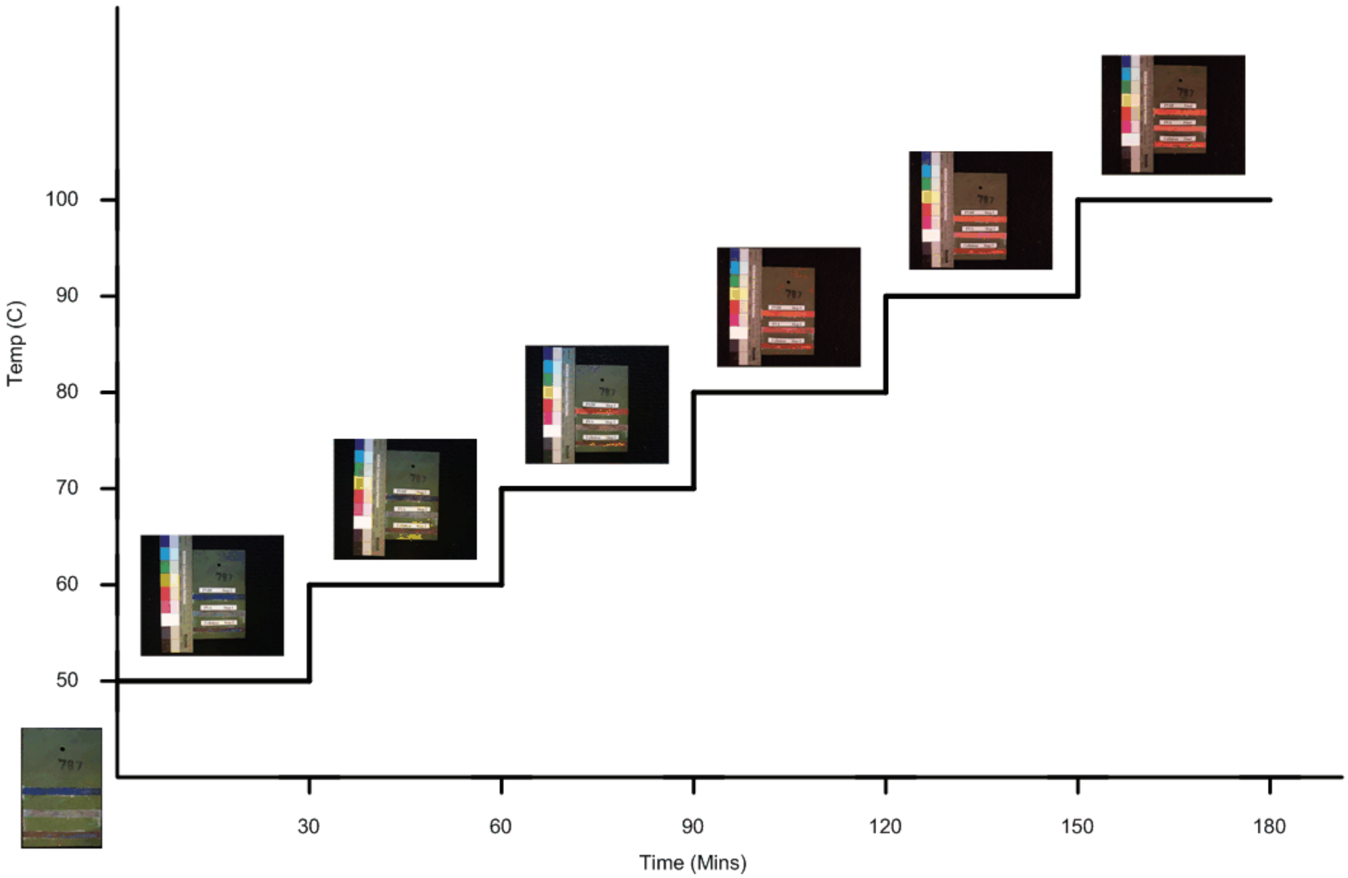

Fig. 9. Thermally induced change over time for panel 787 with 3 bands of thermal indicating paints

The information gained during testing helped optimize the base formulation for blue to red transition each of the desired temperature ranges.

Current base formulations have been developed for prototype coatings within the desired temperature bands. For Band 1, 145°F - 164°F, the formulation comprises of Diacetylene (1:1 PCDA-Bis-1) + TiO_2 + PVP + polymethyl methacrylate (PMMA) with cellulose. For Band 2, 165°F - 184 °F, the formulation comprises of: PCDA + Al_2O_3, TiO_2 + PVP + PMMA with cellulose. For Band 3, over 185°F, the formulation comprises of: PCDA + PVP + ZnO with cellulose.

Since many ammunition items have a lifetime of 15 – 20 years or more, the applied active coating must be able to function reliably over comparable periods of time. The developed coatings and paints must also be suitable for use in all operational environments, including PREPO (preposition storage), depots, and battlefields.

In order to survive in harsh environments, additives common in the paint industry are mixed into the base formulation of the paints to optimize the coating system. ZnO, titanium dioxide (TiO_2), PMMA, etc. are added as ultraviolet-blockers while polyurethanes and fuming silica are added to improve the texture and adhesion of the coatings. The ingredients are mixed by blending and sonication to form paints of various compositions. Surfactants, and in some cases fuming silica, are added as necessary to improve the stability and consistency of the paints. Barium sulfate, fumed silica, cyclodextrin, and nanocrystalline (nc) ZnO improve paint homogeneity and smoothness. Polymers, such as PVDF, PVA, polyurethane and PVP improve paint homogeneity and increase the durability of the paints

Partial reversibility of the red to a purple PDA phase is introduced by the addition of nanosized ZnO and is used to visually and optically monitor the cumulative time within a particular temperature range. This provides both accurate visual cumulative time information as well as quantitative cumulative time information using easy-to-use optical density read-out technology. Cumulative time of exposure in multiple temperature bands can be sensed and optically detected by mixing small amounts of time-temperature sensitive diacetylene monomers into the coating matrices.

Radiation monitoring is being developed using colorless PCDA monomer with the active coatings. The coating is monitored for color changes because the coating becomes blue due to polymerization induced by radiation. The duration of temperature and radiation exposure will be measured by the time-temperature monitoring of the optical density of the coating in the visible spectral range.

Besides typical paint applications, the thermal paints can be separately "packaged" rather than being applied directly to an item. For example, decals containing thermochromic materials will be fabricated and used in applications where paints are impractical or for already-fielded systems.

CONCLUSIONS

In summary, current theaters of operation dictate the need for a real time, rapid assessment of temperature exposure of certain classes of ammunition. Having an indication of the environmental exposure history of an item will enable troops and munitions managers to readily identify ordnances that may have been compromised. The use of thermally active paint systems accomplishes these objectives and assists the development community to address potential vulnerabilities. Furthermore, through the use of a hand held laser scanning device or an optical densitometer, surveillance personnel may be able to assess the duration of this exposure thereby quantifying the effects and better predicting the remaining shelf-life of munitions.

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